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Applicant:	Jens Martin PAULSEN, et al.	)
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		)
For:	LITHIUM TRANSITION METAL OXIDE WITH GRADIENT OF METAL COMPOSITION	)

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Applicants hereby claim the benefits of the filing date of October 31, 2002 to New Zealand Patent Application No. 520452 under provisions of 35 U.S.C. 119 and the International Convention for the protection of Industrial Property.

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Respectfully submitted,

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This certificate is issued in support of an application for Patent registration in a country outside New Zealand pursuant to the Patents Act 1953 and the Regulations thereunder.

I hereby certify that annexed is a true copy of the Provisional Specification as filed on 31 July 2002 with an application for Letters Patent number 520452 made by Jens Martin Paulsen.

I further certify that the Provisional Specification has since been post-dated to 31 October 2002 under Section 12(3) of the Patents Act 1953.

Dated 5 November 2003.

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520452

Patents Form No. 4

Provisional Specification

New Zealand Patents Act 1953

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31 JUL 2002

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Title: *Must be the same as the title on the Application for Patents (Patents form 1)*

ANION CONTAINING MIXED HYDROXIDES AND LITHIUM TRANSITION METAL OXIDE WITH GRADIENT OF METAL COMPOSITION

Applicant: *State (in full) name, address, and nationality of applicant or applicants*

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do hereby declare this invention to be described in the following statement: *(continue application on page 2)*

Please submit this form with the Application for Patent (Patents Form 1)

POST-DATED UNDER SECT. 12(3)

TO 31 OCT 2002

Anion containing mixed hydroxide and lithium transition metal oxide with gradient of metal composition.

This invention relates to a primary material, which is a mixed transition metal hydroxide, mixed oxohydroxide or oxide, having a gradient of metal stoichiometry, containing an anion. The transition metal dominantly consists of manganese, nickel and cobalt, additionally it may contain further metals like Al, Mg, Ti, Cr, B, Ca etc.. The primary material is a suitable precursor to prepare a secondary material, which is a lithiated transition metal oxide, free of the anion, having the same transition metal composition with a similar gradient of metal composition. The composition, the gradient of composition and its morphology enable unique and improved properties of the secondary material in a preferred application as cathode material in rechargeable lithium batteries. Typically the secondary materials are layered lithium transition metal oxides. A preferred (averaged) composition is $Li[Li_xM_{1-x}]O_2$ where $0 \le x < 0.16$, $M=(Mn_uNi_{1-u})_{1-y}Co_y$, $0.4 \le u \le 0.65$ and $0.02 < y < 0.5$, more preferred $0.05 < y \le 0.33$.

A first objective of the invention is a novel lithium transition metal oxide, which, applied as cathode material for rechargeable lithium batteries, exhibits an improved performance. The improved properties originate from the gradient of transition metal stoichiometry which varies gradually from the inside to the outside of a representative particle. Conventional art describes many different cathode materials, generally the cathode materials have a composition, which is the same near to the outside and inside of a representative particle. The optimum composition is a compromise between many different requirements, like cost, processing and performance/properties. The requirements for performance/properties are not the same near to the outside and inside of the particle. Therefore conventional materials with a constant stoichiometry do not represent the optimum regarding cost, processing and properties. An objective of the invention is an improved lithium transition metal oxide powder where a representative secondary particle has a gradient of metal composition, varying smoothly from the outside to the inside of the particle. The novel secondary materials have a better performance as cathode material than a conventional material having the same (average) composition without gradient. Alternatively, the novel materials allow obtaining the same performance at lower materials cost. Thus it is apparent that the secondary materials lithium transition metal oxides with a gradient of metal composition deliver properties and cost advantages which cannot be obtained with conventional art.

A second objective of the invention is a novel precursor material, which is an optimized precursor to prepare the novel secondary lithium transition metal oxide having a gradient of stoichiometry cheap in high quality. The precursor materials are hydroxides, oxohydroxides or oxides having the same metal composition and a similar gradient of metal composition, varying from the outside to the inside of the particle.

A third objective of the invention is a novel primary material, from which the precursor material can be obtained by drying or heating or alternatively, by drying or heating after an appropriate ion exchange process to modify or remove the anion. The primary material is a mixed hydroxide or oxohydroxide, containing an anion. The metal composition and the gradient of metal composition are essentially the same in the primary material, the precursor material and the secondary material.

A fourth objective of the invention is a process, which allows preparing the novel primary material. The process is a precipitation reaction where the composition of the transition metal flow varies in time. It is a further objective of the invention to deliver the primary material, the precursor and the secondary material with a preferred morphology. A preferred morphology of the secondary lithiated transition metal oxide is a powder consisting of secondary particles with approximate spherical shape, the secondary particles being stable aggregations of primary grains. A representative particle has a gradient of metal composition, gradually varying between a composition "A" inside of a primary grain in the center of the secondary particle to a composition "B" at the outside of a primary grain located at the

outside of a the secondary particle. Preferably, a representative secondary particle o also has a gradient of porosity, being minimum in the center and maximum near to the outside.

A further objective of the invention is a primary or precursor material, having a gradient of metal composition, which could have use in further applications, for example as cathode in alkaline batteries. One possible example follows. Ni-Mn hydroxide itself could have a potential application (for example as cathode for an alkaline cell), this application is however limited by the solubility of manganese in the electrolyte at high pH. Here a mixed hydroxide having a gradient with Ni-Mn hydroxide in the center, protected by $Ni(OH)_2$ at the surface can be desired.

Summarizing, this invention discloses primary materials which are anion containing mixed transition metal hydroxides or oxohydroxides, and it discloses precursor materials, being hydroxides, oxohydroxides or oxides prepared from the primary materials, during the preparation the anion might be modified. The precursor materials are used to prepare secondary materials having a preferred morphology, being lithium transition metal oxides, free of the anion. The primary, precursor and secondary materials have essentially the same transition metal composition, and they all have a similar gradient of metal composition.

A typical preparation occurs in several steps: First, the primary material, the anion containing hydroxide is prepared by a constant pH precipitation. During precipitation, the composition of the metal salt flow is varied. Second the precursor material is prepared from the primary material applying drying or heating. In special implementations the anion is modified by an ion exchange reaction followed by drying or heating. Finally the secondary material is prepared by reacting a source of lithium with the precursor material, followed by a sintering to densify the cathode.

I a preferred implementations a particularly dense primary material is achieved by applying a constant pH precipitation using more than one volume. The process is characterized by inserting a flow of dissolved metal salt (like $M\text{-}SO_4$) with flow rate "x" into a volume "α" which has a lower pH, and inserting a flow of base (like NaOH) with flow rate "y" into a volume "β", which has a higher pH. The volumes are connected by at least one connection which enables to transfer precipitated hydroxide dispersed in salt solution from volume "α" to volume "β" with a flow rate "Z" and to transfer precipitated hydroxide dispersed in salt solution from volume "β"to volume "α" with a flow rate "Z'". Otherwise the volumes are separated to prevents an immediate and complete mixing of the volumes "α" and "β" by too large flows "Z" and "Z'". The process is furthermore characterized that the pH in both volumes is kept within preferred regions, being not the same in both volumes. Preferred regions, being about 7-10 in "α" and between 10 and 11.5 in "β".The volumes "α" and "β" can be separated (to limit "Z" and "Z'") regions of the same vessel, or the volumes "α" and "β" are separated vessels, connected by at least one connection (to enables sufficiently limit "Z" and "Z'").In an preferred implementation a flow "u" is removed from the system, and after thickening (removing salt-solution) is fed back. This process increases the time where base and metal sulfate can "soak" into the hydroxide, which lowers the degree of supersaturation of the solution during precipitation, and causes the precipitation of a denser hydroxide. During the precipitation process the composition of the metal flow is varied.

In a further preferred implementation the sintering temperature is lowered and the anion is extracted from the precursor material by utilizing the in-situ formation of secondary salts of high solubility, acting as sintering aids. To achieve this, a primary salt is added before the reaction step. During reaction, the primary salt reacts with the anion to form a secondary salt, which coexist with the secondary material even at the high sintering temperature. I The sintering is made at a temperature above or about being the melting point of the secondary salt. Finally, the salts are removed from the secondary material by a washing and drying step. The lower sintering temperature lowers the processing cost. Additionally, it allows preparing

the secondary materials from precursors with little relaxation of the stoichiometry gradient. It is also beneficial that anion containing precursors can be applied since the removal by an ion exchange reaction with hydroxide "curing" is less effective and causes additional cost.

In a special implementation of the invention the wet primary material is kept in contact with CO_2 gas. This can be achieved during filtering. The CO_2 probably exchanges with sulfate to form sulfuric acid. This allows some "melting" and de-watering of the particles which cause a densification and improve the density of final Li-M-O_2.

In a further implementation of the invention the anion composition of the primary material is modified. If for example during precipitation some chloride ions (additionally or instead) of the sulfate ions are supplied, then the anion contain chloride.

Conventional art describes coating to improve the properties of cathode materials. Generally only a very thin outer layer of the particles is coated, typically in a separated "wet" step, followed by a mild heating. Coating is done to protect the surface for example to avoid an unwanted oxidation of the electrolyte during overcharge. Usually the coating is on the surface of the particles, or it may penetrate into the outermost layer of the particles, thus the bulk properties are not or only little modified. Coating as described in previous art does not allow to fully optimize the cathodes and generally it does not allow to lower the cost.

Compared to $LiCoO_2$, cathode materials, basing on $LiNi_{1/2}Mn_{1/2}O_2$ tend to have a lower kinetics of the lithium transport by diffusion in the solid phase. $LiCoO_2$ with a low BET surface area (< 0.5 m^2/g) still support high rates, whereas $LiNi_{1/2}Mn_{1/2}O_2$ based materials with low surface area do not, apparently this phenomena is related to the lower lithium-diffusion kinetics. The conventional approach to optimize $LiNi_{1/2}Mn_{1/2}O_2$ is to allow a larger BET surface area, resulting in shorter diffusion lengths and a better rate performance. This approach however makes it difficult to obtain materials with a sufficient high tap density (or pressed density) to achieve sufficient high electrode densities. Another conventional approach describes the introduction of additional cobalt doping to improve the lithium diffusion kinetics. It might however desired to keep the cobalt doping level low.

A careful theoretical investigation of lithium transport in the solid phase will show that it is desirable to have a good Lithium transport kinetics on the outside of primary particles on the outside of the secondary particles. At the inside of primary particles, especially in the inside of the secondary particles a lower transport kinetic can be tolerated. This is justified by the fact that the effective transport rates of lithium during charge or discharge reduce from the outside to the inside of primary and secondary particles, finally reaching Zero at the point where the radial diffusion "fronts" meet. Due to the desire to keep the cobalt content low it would be preferable to establish a gradient of cobalt content, being rich in cobalt at the outside, and poor in cobalt at the inside. Such a particle is an optimized compromise between a low total cobalt doping level and high effective lithium transport kinetics. The lithium diffusivity is at its maximum at the outside and at its minimum at the inside of the particle.

$LiNi_{1/2}Mn_{1/2}O_2$ based materials have a lower electronic conductivity than $LiCoO_2$. A good electronic conductivity across the positive electrode in a battery is required to support high rates and keep the polarization low. The electronic electrode-conductivity is improved by adding conductive additives like carbon black to the electrode. To keep processing cost low, to enable a high volume density, and to allow for a sufficient electrolyte filled porosity (to enable for the fast transport of lithium across the electrode in the liquid phase) preferable the amount of carbon additive is as low as possible. $LiNi_{1/2}Mn_{1/2}O_2$ based materials will generally tend to require larger loadings of conductive additive and they will be more sensitive to non-optimized electrode processing. This is due to the lower electronic conductivity. The electronic conductivity can be improved by modifying the material by doping. The electronic conductivity tends to improve if the doping level of cobalt is increased.

Anion containing mixed hydroxide and lithium transition metal oxide with gradient of metal composition.

A careful theoretical investigation of the electronic conductivity of an electrode gives the result that it is sufficient, if only the outer layer of primary particles, especially at the surface of the secondary particles have a good electronic conductivity. A lower electronic conductivity in the inside of primary particles, especially in the center of secondary particles can be tolerated. Due to the desire to keep the cobalt content low it would be preferable to establish a gradient of cobalt content, being rich in cobalt at the outside, and poor in cobalt at the inside. Such a particle is an optimimum compromise between low total cobalt doping level and high electronic conductivity at the outer surface of primary particles at the outside of secondary particles, thus generating an improved effective electronic conductivity across the electrode.

An optimum cathode powder consists of secondary particles having spherical shape. This simplifies the processing of the powders in the coating step, and spherical particles deliver electrodes with high density and straight porosity with low turtoisity, which is desired to enable a fast transport of lithium in the liquid phase across the electrode. Preferably, the spherical secondary particle consists of primary particles, arranged so that a sufficient interconnected porosity into the inner of the particle with low-turtoisity-remains. The transport kinetics of lithium in the electrolyte is much faster than in the solid. In the case of a sufficient porosity the typical diffusion length for the diffusion of lithium in the solid phase is about the size of the primary particle. If the electrolyte filled porosity is too low, then the solid phase diffusion length is about the size of the secondary particle. A careful theoretical investigation of the lithium transport in porous spherical particles shows that a gradient of porosity is desirable. The optimum compromise between high tap density and sufficient open porosity is obtained by spherical secondary particles which have a gradient of porosity – with a maximum porosity at the outside and the minimum porosity at the inside. The reason is that the rate of lithium transport in the liquid phase decreases from the outside to the inside, finally reaching zero at the central point where the diffusion fronts meet.

Surprisingly it was observed that the coprecipitation of mixed $Ni_{1/2}Mn_{1/2}$ hydroxide delivers hydroxide with a high tap density, whereas cobalt containing mixed $(Ni_{1/2}Mn_{1/2})_{1-x}Co_x$ hydroxide, had an decreasing tap density with increasing levels of cobalt. The denser $Ni_{1/2}Mn_{1/2}$ hydroxide consists of spherical secondary particles, consisting of small primary particles where the primary particles are arranged so that the porosity is low, resulting in a large tap density. Introduction of cobalt causes an arrangement of primary particles with larger porosity. Apparently, an increase of cobalt contents during prepipitation allows preparing mixed hydroxides with the desired gradient of porosity. The gradient basically remains during a moderate sintering. Thus a gradient of cobalt doping, having the maximum cobalt content at the outside and the minimum at the inside can establish the preferred cathode particle-morphology showing the desired gradient of porosity with the maximum porosity at the outside of the secondary particles.

In a further implementation of the invention it is preferable to have a gradient of composition to obtain an optimized safety of the cathode. Better safety can be obtained by doping with Al or MgTi, or by a high concentration of Mn. These dopands may eventually be "inert", i.e they do not contributing to the capacity. In this case it is preferable if the concentration reduces from a maximum at the surface of a primary particle at the outside of the secondary particle to a minimum at the inside of a primary particle at the center of the secondary particle.

It can be summarized that the preparation of a cathode powder, consisting of spherical secondary particles having a gradient of composition is desirable. Suitable precursors have the same gradient, and are prepared from suitable primary materials again having the same gradient. In a special implementation of this invention the cobalt content is varied. A gradient with a maximum doping level at the outside allows to achieve all benefits with lower absolute levels of cobalt, and additionally, allows to obtain a desired morphology with a gradient of

porosity, allowing to achieve improved electrode densities. Dopands, which improve the safety, should show a similar gradient.

Conventional art teaches that lithium transition metal oxides with complex metal composition have improved properties. Examples are materials like $Li[Li_xM_{1-x}]O_2$ with $x\cong0.05$ and $M=(Mn_uNi_{1-u})_{1-y}Co_y$, $0.4 \leq u \leq 0.65$, $0.1 \leq y \leq 0.3$ demonstrated by Ilion or $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ as demonstrated by Ohzuku. Ilions patent concludes that a cobalt level of $0.1 < x < 0.3$ is needed, whereas a level of about $x=0.16$ is most preferable in $Li[Li_yM_{1-y}]O_2$ with M being $(Ni_{1-z}Mn_z0_{1-x}Co_x$. The actual presented invention allows to reduce the total level of cobalt. Good cathode material can be achieved with a total $x<0.1$. Additionally it allows to effectively improving the safety by introducing effective dopands like Al but keeping the total doping level low due to the implementation of the gradient.

During the reaction of a mixed hydroxide together with a source of lithium, the morphology of the hydroxide will change only little. During sintering the primary particles tend to sinter towards denser aggregates and the shape of the secondary particles remains. Densification by sintering is essential to obtain cathode powders with high tap or press density. If the density is not sufficient, then the battery will suffer from less volumetric energy density. The densification occurs by a diffusive transport of cations and anions driven by differences in surface tension. Lithium (and probably oxygen) diffuses fast, the diffusion of cations like transition metal and of other dopands like Al or Mg is slow. Also the diffusion which relaxes the gradient of metal stoichiometry is slow. The latter requires a diffusion with a typical diffusion length in the order of the radius of the secondary particle. Contrary, the processes causing a densification of the particle, have a typical length of diffusion in the order of the radius of the much smaller primary grains. Since the fist diffusion length is about/more than 10 times larger then the second, a typical relaxation time of the first process (assuming the same driving force) is more than 100 times slower. This allows achieving a densification of the particles with only a partial lowering the gradient of metal stoichimetry. The use of molten salts as sintering agents (preferably formed in-situ) can further reduce the relaxation of the gradient during sintering. Sintering aids like molten salts are effective to supply a faster diffusion parallel and near the interface of molten salt and solid, which causes the densification but it does not increase the kinetics of the bulk diffusion, which causes the stoichiometry gradient relaxation.

In the following a list of possible implementations of this invention is given

1. A mixed transition metal hydroxide containing an anion with an averaged composition of $M(OH)_{2-2a-b}X_aX'_b*(H_2O)_n$ containing particles with a gradient of stoichiometry where
   X is a divalent anion comprised of one ore more chosen from SO_4^{2-} and CO_3^{2-} and
   X' is a monovalent anion dominantly being Cl^- and
   $0.1 < 2a+b < 0.3$ and
   $n > 0$
   where M is $(Mn_uNi_{1-u})_{1-y-z}Co_yA_z$ where
      $0.4<u<0.65$
      $0 < y < 0.67$
      A is any one of ore mixtures of Al, Mg, Ti, Ca, B, Zr, RE with $0 < z < 0.1$
   the gradient of stoichiometry is
      a gradient of transition metal composition or/and
      a gradient of A

2. Hydroxide of example 1 with X' being Cl^- and $b > 0$, prepared by constant pH precipitation in the presence of some Cl^- ions.

3. Hydroxide of example 1 with X being CO_3^{2-} and b≅0 prepared by constant pH precipitation followed by an ion exchange reaction in a CO_3 containing liquid like Na_2CO_3

4. Hydroxide of example 1 with a≅0, b≅0 prepared by constant pH precipitation followed by a repeated ion exchange reaction in a OH^- containing liquid ("curing"), like NaOH or LiOH

5. A constant pH precipitation process to prepare the hydroxides of example 1 to 4 by inserting a flow of metal salt (like $M\text{-}SO_4$) and a flow of NaOH into at least on reaction vessel kept within at least one preferred pH region. The M composition of flow 1 changes in time.
   5A) two vessels being kept at different preferred pH, the vessels are connected to enable a controlled mixing between the dispersions in both vessels
   5B) One vessel within a preferred pH region.
   Preferable at 70-90°C, preferable the dispersion is thickened during precipitation, preferable the vessels are in laminar motion (obtained by stirring), preferable the flows have a concentration of 1-2.5 M (metal salt) and 2-5M (base), eventually additional NH_4 (for exampel as $(NH_4)_2SO_4$ is added with a stoichiometric flow ratio NH_4 : M being about 0.2 : 1.

6. An mixed transition metal hydroxide according one of the claims 1-4 which was separated from the solution (for example by filtering) in the presence of a CO_2 atmosphere.

7. A mixed transition metal oxohydroxide precursor, containing an additional anion X or X' with an averaged composition of $MO_k(OH)_lX_aX'_b*(H_2O)_n$ or mixed transition metal oxide (l=0, n≅0) with a gradient of stoichiometry
   where $1 < k+l < 2$ and
   where X is SO_4^{2-} and
   where X' is Cl^- and
   where $0.1 < 2a+b < 0.3$ and
   where $0 \leq n < 1$ and
   where M is $(Mn_{1-u}Ni_u)_{1-y-z}Co_yA_z$ where
   $0.4<u<0.65$
   $0 < y < 0.67$
   A is any one of ore mixtures of Al, Mg, Ti, Ca, B, Zr, RE with $0 < z < 0.1$
   prepared from the hydroxide of example 1-4 or 6 by drying or heating.

8. A lithiated transition metal $Li_{1+x}M_{1-x}O_2$ with $0<x<0.16$ with an stoichiometric gradient
   where M is $(Mn_{1-u}Ni_u)_{1-y-z}Co_yA_z$ where
   $0.4<u<0.65$
   $0 < y < 0.67$
   A is any one of ore mixtures of Al, Mg, Ti, Ca, B, Zr, RE with $0 < z < 0.1$
   the gradient of stoichiometry is
   a gradient of transition metal composition or/and
   a gradient of A

9. A lithiated transition metal $Li_{1+x}M_{1-x}O_2$ with $0<x<0.16$ with an stoichiometric gradient
   where M is $(Mn_{1-u}Ni_u)_{1-y-z}Co_yA_z$ where
   $0.4<u<0.65$
   $0 < y < 0.67$

A is any one of ore mixtures of Al, Mg, Ti, Ca, B, Zr, RE with $0 < z < 0.1$
the gradient of stoichiometry is
a gradient of transition metal composition or/and
a gradient of A
prepared by reacting the precursor mixed hydroxide according cone of the examples 1-4, 6-7 with a source of lithium at elevated temperature.

10. Same as 9, followed by a sintering step.

11. Secondary material of example 10 prepared from an anion containing precursor. Before the reaction step a primary salt is added. The primary salt reacts with the anion to form a highly soluble secondary salt, coexisting with the secondary material and acting as sintering aid. After the sintering the secondary material is washed and dried.
 11A) The anion is SO_4^{2-}, and the anion is transferred to a secondary salt Li_2SO_4 by using an excess of Li_2CO_3
 11B) The anion is SO_4^{2-}, and the anion is transferred to secondary salts Li_2SO_4 and Na_2SO_4 by a small excess Li_2CO_3 and additional Na_2CO_3
 11C) The anion is Cl^- and the is transferred to secondary salts LiCl and using excess of Li_2CO_3 and additional Na_2CO_3
 11D) The anion is Cl^- and the is transferred to secondary salts LiCl and NaCl by a small excess Li_2CO_3 and additional Na_2CO_3
 11E) The anion is CO_3 and is transferred to a secondary salt K_2CO_3 by using a small excess of Li_2CO_3 and additional KOH
 11F) One of 10A-10E and additional NaCl is added.

12. The secondary material of example 9 having not only a gradient of metal composition but also a gradient of porosity.

13. A lithiated transition metal $Li_{1+x}M_{1-x}O_2$ with $0<x<0.16$ with an stoichiometric gradient where M is $(Mn_{1-u}Ni_u)_{1-y-z}Co_yA_z$ where
 $0.4<u<0.65$
 $y=0.33$
 the gradient of stoichiometry is a gradient of cobalt composition changing from about 0.16 in the center to about 0.5 at the outside

14. A lithiated transition metal $Li_{1+x}M_{1-x}O_2$ with $0<x<0.16$ with an stoichiometric gradient where M is $(Mn_{1-u}Ni_u)_{1-y-z}Co_yA_z$ where
 $0.4<u<0.65$
 $y=0.08$
 the gradient of stoichiometry is a gradient of cobalt composition changing from about 0.05 in the center to about 0.17 at the outside